The Effect of Fillers upon Degradation of Poly(organosiloxane) Rubbers*

R. M. ASEEVA, A. A. BERLIN, and S. M. MEZHIKOVSKY

Institute of Chemical Physics, Academy of Sciences of the USSR,
Moscow

The effect of silica fillers upon thermal and oxidative thermal degradation of poly(dimethyl vinylsiloxane) rubber has been studied. The silica fillers have been found to deactivate terminal hydroxyl groups of polymer and to inhibit the chain oxidative process of organic substituents, besides promoting the observation of heterolytic cleavage of siloxane bonds. The role of active centres on the silica surface has been determined. The kinetic parameters of the oxidative thermal degradation of the polymer *vs.* the fillers concentration have been determined.

The highly disperse silica fillers are widely used for reinforcing the poly(organosiloxanes) (POS) and preparing the materials on their basis.

The problem of polymer—filler interaction and its effect upon various properties of filled polymers is fundamental. But up to the present time it has yet received no appropriate developing. Most of the papers published on this subject concern the factors, which determine the reinforcing ability of POS fillers [1]. Information on filler effect upon thermal stabilities of both the POS rubbers and the vulcanizates is limited and is generally qualitative [2, 3].

The present study is concerned with the effect of highly disperse silica fillers upon the oxidative thermal degradation kinetics of poly(dimethyl vinylsiloxane) rubber. An attempt was made to elucidate the dependence between physicochemical properties of the fillers and their influence on the rubber thermal oxidation.

Experimental

Poly(dimethyl vinylsiloxane) rubber SKTV ($M_v = 5 \times 10^5$) prepared in the presence of acid catalyst was investigated. The substitution of —OH terminal groups in SKTV rubber by trimethylsiloxy groups was carried out according to the procedure described in [4]. There were no —OH groups left in the rubber.

The powdered silica trademark Y-333 (obtained by precipitation of aqueous sodium silicate solutions with acid) and Aerosil (obtained by combustion of silicon tetrachloride under stream of hydrogen) were studied as fillers.

Table 1

Characteristics of the fillers

No.	Filler	Specific surface [m² g⁻¹]	pH	Weight losses [%]				Bands in i.r. spectra [cm⁻¹]
				120°C	300°C	450°C	600°C	
1	Y-333	34.3	6.2	5.3	7.2	7.3	7.5	3750, 3400, 1640
2	Aerosil	154.9	4.4	1.75	4.0	5.3	6.8	3750, 3650, 3450, 2350, 2030, 1640
3	modified Aerosil	150.0	6.2	0.25	2.0	4.0	6.2	3750, 3650, 3400, 2940, 2350, 2030, 1860, 1640, 1420

For elucidating the role of functional groups on the filler surface, Aerosil modified with saturated vapour of trimethylchlorosilane was used. The extent of the modification of the surface was approximately 70%.

Table 1 shows some parameters of the fillers.

Specific surface was determined by BET method from nitrogen sorption. Weight losses of fillers in air were determined at heating rate 3 degree per 1 minute on a Derivatograph of F. Paulik, J. Paulik, and L. Erdey.

The rubber-filler mixtures were prepared by mixing the components at room temperature in microroller. Degradation kinetics was studied with thermogravimetric method *in vacuo* (10^{-4} mmHg) using automatic BTB-2 balance and in air by means of a Derivatograph. In all experiments the weights of samples were no more than 100 mg. Effective parameters of degradation kinetics were estimated according to [5].

Results and Discussion

Fig. 1 shows the TG curves of both poly(organosiloxane) rubber and its mixture with 20 wt. parts of Y-333 measured *in vacuo*. For a comparison TG curves are presented for degradation of rubber in which the hydroxyl terminal groups of macromolecules are
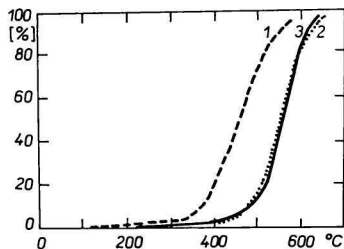

Fig. 1. The TG curves of SKTV degradation *in vacuo*.
Heating rate 3 degree/min.

1. SKTV; *2.* SKTV with 20 wt. parts of Y-333 (based on the polymer); *3.* SKTV with blocked terminal groups of macromolecules.

substituted by trimethylsilyl ones. As seen from Fig. 1 on introduction of 20 wt. parts of powdered Y-333 silica the starting temperature of intensive degradation (Td) of the polymer is shifted by almost 100°C. The increase of Y-333 silica content to 40 wt. parts caused practically no change in Td. It is interesting to note that in the case of rubber with blocked terminal groups an addition of 20 wt. parts Y-333 silica has no effect on the value of Td. Thus the influence of Y-333 silica (20 wt. parts) upon thermal degradation of SKTV is adequate to the effect of the blocking of hydroxyl terminal groups of SKTV macromolecules. Apparently a specific interaction of POS with silica surface is responsible for a deactivation of depolymerization centres in the rubber. A mechanism of such interaction is yet uncertain.

Degradation of POS is very complicated in the presence of oxygen.

A general character of degradation kinetics is determined by a competition between the degradation of the main polymer chain and the reactions of its substituents. On the basis of the experimental data it has been assumed that the free-radical chain oxidation of the siloxane skeleton organic environment facilitates the polymer crosslinking, formation of active POS depolymerization centres and accelerates formation of the volatile products. Its initiation occurs in accord with statistical law or on the weakest bonds [6].

The highly disperse silica fillers affect in different manner the POS thermal oxidation kinetics. As an example the derivatograms of the mixtures of SKTV with 10 and 30 wt. parts Y-333 silica are shown in Fig. 2a.

Up to a certain concentration (~30 wt. parts per 100 wt. parts of the polymer) the powdered Y-333 silica causes a shift to high temperature of both Td and starting temperature of an exothermic peak in DTA curve associated with an organic radical oxidation and crosslinking. Such peak has not been revealed in the oxygen free system. We assume that the silica filler inhibits the oxidation and crosslinking of POS chains since the intensity and the position of exothermic peak at 300—400°C changes when Y-333 silica.
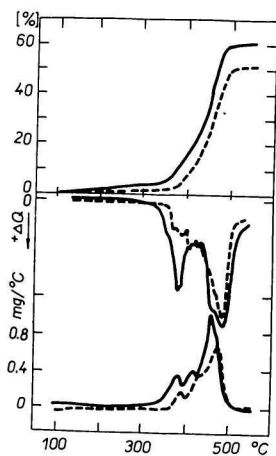

Fig. 2a. The derivatograms of mixtures of SKTV with 10 wt. parts (———) and 30 wt. parts Y-333 (— — —).
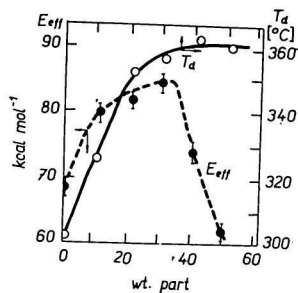
Fig. 2b. The effect of Y-333 silica concentration on E_{eff} and Td.

content in the mixtures is increased. The POS thermal oxidation and the volatile products formation proceed in several stages. The DTG and DTA curves (Fig 2a) point to the existence of a few overlapping stages in the overall decomposition process. Effective kinetic parameters of weight losses for the stage specified by an intensive interaction between oxygen and methyl groups of the polymer (300—440°C) were estimated from the TGA data. Fig. 2b shows the effect of Y-333 silica content upon the change of effective activation energy and Td of the polymer.

The high E_{eff} for POS thermal oxidation is probably connected with a contribution of the purely thermal processes to the weight losses. Fractional reaction order varying within 1.4—2.5 with filler content also indicates that the mechanism of SKTV thermal oxidation is complicated.

As seen from Fig. 2b the increase in Y-333 silica content to ~30 wt. parts considerably increases the E_{eff}.
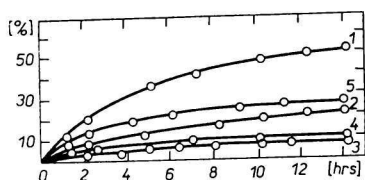

Fig. 3a. Effect of filler on kinetics of thermal oxidation at 300°C.
1. pure SKTV mixtures filled with Y-333;
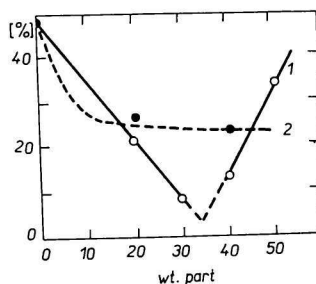2. 20 wt. parts; 3. 30 wt. parts; 4. 40 wt. parts; 5. 50 wt. parts.

Fig. 3b. Weight losses of polymer component of the mixtures after the ageing in air at 300°C.
1. with Y-333 for 10 hours; 2. with Aerosil for 30 hours.

Extreme character of the SKTV weight loss vs. the Y-333 silica concentration is again observed at ageing the samples in air under isothermal conditions at 300°C (Fig. 3a, b). Thus in order to increase oxidative thermal stability of the POS mixtures one should work with optimal silica concentrations.

When the filler concentration is above optimum the negative effect of Y-333 filler upon the propagation of polymer degradation is distinctly pronounced.

The negative influence of Y-333 silica filler when its content in mixture is sufficiently high is pronounced not only in the change of weight losses but it appears also in the change of elastic and other physicochemical properties of the system.

Different behaviour is observed in thermal oxidation of SKTV mixtures filled with Aerosil (Fig. 3).

10 wt. parts of Aerosil is sufficient to attain a limiting decrease of weight losses in SKTV, while its Td increases only by 5—7°C.

In respect to Y-333 silica, Aerosil being the more active reinforcing filler is rather weak to suppress the oxidation of organic substituents.

The character and properties of the silica fillers surface (in particular the nature and the concentration of active centres) are very important for the oxidative thermal stability of POS mixtures. This can be seen from a comparison of the data on thermal oxidation

of SKTV samples filled with modified Aerosil and Y-333 silica preliminary treated at 600°C for 6 hours. Such treatment resulted in almost no change of the specific surface of Y-333 silica. However, its surface "quality" changed essentially with the removal of moisture adsorbed, hydroxyl group cleavage from surface and bulk, partial destruction of a crystalline lattice in the siloxane skeleton of silica and due to some other high temperature processes. Fig. 4a shows the effect of Y-333 treatment upon the SKTV thermal oxidation at 300°C. A freshly prepared silica sample acts as a catalyst of SKTV degradation. Probably the strained siloxane bonds

$$\underset{\text{Si} \qquad \text{Si}}{\overset{O^*}{\diagup \quad \diagdown}}$$

appearing after dehydration
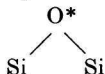
in the course of calcination are more easier to cleave at high temperatures of POS ageing. Such strained bridges and the cleaved $-\overset{|}{\underset{|}{Si}}^+$ and $^-O\overset{|}{\underset{|}{Si}}-$ bonds on the surface of filler may be the centres accelerating the poly(organosiloxane) degradation. Chemical relaxation and rehydration of a calcinated silica sample decrease the number of such centres. At long exposition to the humid medium (in desiccator over calcinated calcium oxide) the primary surface characteristics of Y-333 could be resumed.
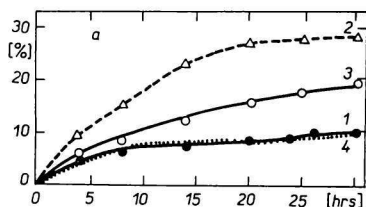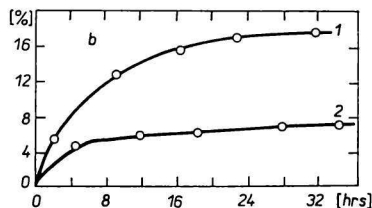

Fig. 4. Kinetics of thermal oxidation (at 300°C) of SKTV mixtures filled with 40 wt. parts of:

a) silica Y-333: *1.* initial; *2.* thermally treated at 600°C; *3.* the same as in *2* but after 1 month; *4.* after 3 months' exposition in desiccator.

b) Aerosil: *1.* initial; *2.* modified.

As seen from Fig. 4a a mixture with silica sample stored in desiccator for 3 months shows oxidative thermal stability identical to that observed with the untreated silica.

The effect of filler surface properties upon the course of polymer degradation can be also determined from a comparison of SKTV mixture containing Aerosil and its modification (Fig. 4b).

The substitution of hydroxyl groups of silica surface by trimethylsilyl ones enhances essentially the polymer oxidative thermal stability. In the presence of 40 wt. parts of modified Aerosil Td of SKTV is almost 50°C above that observed with ordinary Aerosil.

In order to understand such effects of silica fillers one should be more attentive to the analysis of surface properties of silica and to discussing the process of POS thermal oxidation in the light of various factors.

According to the modern conceptions the free hydroxyl groups behave as active centres of the sorption of various compounds on the surfaces of silica and other oxides [7]. In particular, a direct relationship has been established for the amount of physically adsorbed water and the content of surface hydroxyl groups. From the quantity of moisture removed *in vacuo* one may roughly estimate a content of hydroxyl groups on the surfaces of filler samples [8]. The stabilizing properties of the latter depend upon their specific surfaces and particle sizes as well as on a surface concentration of hydroxyl groups. As concentration of the latter per 1 m² of the surface decreases, a reinforcing effect of the filler enhances in the sequence: Y-333 (1.54×10^{-3} g/m²) < Aerosil (1.13×10^{-4} g/m²) < < modified Aerosil (1.67×10^{-5} g/m²). There is no direct correlation between the rein- forcing properties of fillers and their effect on the oxidative thermal stability of poly(orga- nosiloxanes). But the presence of hydroxyl groups capable to act as centre of the sorption of moisture and the polymer molecules is also important in POS thermal oxidation. It is known that the cleavage of siloxane bonds in the organosilicon elastomers can proceed *via* heterolytic mechanism [9]. The hydroxyl groups on the surface of silica are of acid character. The acid centres of the filler facilitate the depolymerization of the poly(orga- nosiloxane) rubbers.

As seen from Table 1, after the substitution of hydroxyl groups of silica surface by trimethylsilyl ones the acidity of filler decreases, but the stability of mixture increases.

In the presence of a large amount of the filler the concentration of acid centres enhan- ces and the conditions of oxygen penetration into the bulk sample become worse. Under these conditions the contribution of the depolymerization processes to the thermal oxi- dation of poly(organosiloxane) rubber increases too.

The filler acts as a nucleating agent affecting in general the relaxation properties of macromolecules.

In turn the change of molecular mobility of poly(organosiloxanes) influences the ele- mentary reaction kinetics in the course of thermal oxidation.

By means of paramagnetic probe method [10] the molecular mobility of POS matrix was shown to decrease with the increasing Y-333 silica content up to ∼ 30 wt. parts. This silica content in rubber mixture is probably sufficient for the formation of unimolecular adsorptive layers of SKTV and creates favourable conditions for complete deactivation of depolymerization centres.

With further increase of Y-333 silica content the increase of deactivation of polymer OH terminal groups cannot be achieved but the concentration of acid or other active surface sides facilitating the SKTV degradation is enhanced. This probably leads to a smaller E_{eff} of the POS degradation as it was found in the present work.

The obtained experimental data indicate that the positive effect of silica fillers on ageing of poly(organosiloxanes) may be associated with inhibiting the oxidation of side radical chains and with deactivation of depolymerization centres.

At the increasing concentration of the filler its negative effect is pronounced, depending on its nature, surface groups activity, and the character of its transformations at high temperatures.

Investigation of the nature of silica and other fillers and their interaction forces with polysiloxane enables to answer many problems concerning an intimate mechanism of filler participation in the thermal oxidative ageing of polymers.

References

1. Warrick E. L., Lanterbur P., *Ind. Eng. Chem.* **47**, 486 (1955).
2. Kuzminsky A. S., Goldovsky E. A., *Dokl. Akad. Nauk SSSR* **160**, 125 (1965).
3. Goldovsky E. A., Kuzminsky A. S., *Kinetics and Mechanism of Polyreactions.* Preprints 11/46, Vol. *V*, p. 369, Budapest, 1969.
4. Andrianov K. A., Slonimsky G. L., Papkov V. S., Yakushkina S. E., *USSR Patent* 228 949 (1968); *Bull. Izobr. SSSR*, No. 32 (1969).
5. Papkov V S., Slonimsky G. L., *Vysokomol. Soedin.* **8**, 80 (1966).
6. Mezhikovsky S. M., Aseeva R. M., Berlin A. A., *Vysokomol. Soedin.* **A15**, 1 (1973).
7. Little L. H., *Infrared Spectra of Adsorbed Species.* Academic Press, London — New York, 1966.
8. Jonag G. J., *J. Colloid Sci.* **13**, 67 (1958).
9. Kučera M., Láníková J., Jelínek M., *J. Polym. Sci.* **53**, 301 (1961).
10. Vasserman A. M., Buchachenko A. L., Kovarsky A. L., Neiman M. B., *Vysokomol. Soedin.* **10A**, 1930 (1968).